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(54) Glass composition for the production of fibres.

(57) Glass fibres can be produced from molten glass com-
positions by various fibrisation processes, but each
process requires a specifically developed glass composi-
tion in order to optimise the amount of wastage, the ex-
pense of the composition, the fluidity and crystallisation
tendency of the melt, and the quality (heavy-weight or
light-weight) and hydrolytic resistance of the glass fibre
product. For example, the process giving a light-weight
product in a high yield requires an expensive composition
that cannot readily utilise industrial wastes. The glass
composition of the invention is suitable for several
processes and can utilise industrial wastes while giving a
light-weight good quality product. The amounts of all
components of the composition are maintained within
specified ranges and the weight ratios CaO : Na$_2$O, SiO$_2$:
Al$_2$O$_3$, K$_2$O : Na$_2$O and (CaO/Na$_2$O) : (SiO$_2$/Al$_2$O$_3$) are also
maintained within given ranges.

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"Glass composition for the production
of fibres"

The present invention relates to a glass composition
for the production of fibres.

The term "glass composition" as used herein means a
composition or mixture of components - whether in the solid

5 state or the liquid state - that is suitable for the manu-
facture of glass, that is to say a composition that can be
solidified from the melt under suitable conditions to pro-
duce glass. Many different materials and mixtures of
materials can be used to manufacture glass but the ease with

10 which the manufacturing process can be carried out and the
quality of the glass so produced depend largely on the par-
ticular glass composition used.

Several processes have been proposed and/or are used
for converting molten glass compositions into glass fibres.

15 Some of these fiberisation processes give better quality
products than do other of the processes but the poorer
quality products are quite suitable for certain purposes.
Moreover, some of the processes can use readily available
inexpensive starting materials, whereas other of the pro-

20 cesses require more expensive starting materials. Several
fiberisation processes that have been or are used are sum-
marised by J. Gilbert Mohr and William Rowe, "Fiber Glass",
Van Nostrand Reinhold Company, New York, 1978. Three of
the commonly used processes are the rock-wool process, the

25 rotary process (also known as the glass-wool process), and
the flame-attenuation process (also known as the glass-
drawing process).

In one variant of the rock-wool process, molten
glass composition is fed onto one or more discs rotating

with a high peripheral speed and the melt is flung by
centrifugal force into a suitably directed and controlled
air stream, where it forms into fibres and cools. The
fibres are carried by the air flow and collected at a
5 suitable point for further treatment. Other variants of
the rock-wool process are the steam-blown process and the
spinning process (see Mohr and Rowe, pp. 9 and 11).

A major disadvantage of the rock-wool process in
general is that only about 40 - 45% of the glass melt is
10 actually converted into fibres. Up to about 25% of the
melt collects as waste, for example by being flung direc-
tly into a waste chamber below the disc(s), and the remain-
der forms into shot of various sizes. The product of this
process thus contains up to about 40% of shot and is there-
15 fore primarily suitable for further processing into heavy-
weight fibre products, such as those products generally
known as rock wool, mineral wool or slag wool. This pro-
cess cannot economically be used for the production of
shot-free light-weight fibre products, such as the product
20 commonly known as "glass wool". (In this respect it should
be noted that although such a light-weight shot-free pro-
duct is commonly known as "glass wool", this term is strictly
a generic term referring to a mat or felt of glass fibres
and includes products such as rock wool, mineral wool and
25 slag wool mentioned above.) An important advantage of the
rock-wool process, however, is that it can utilise inexpen-
sive starting materials, for example fly ash and various
slags.

In the rotary process (also known as the glass-
30 wool process), molten glass composition is fed into a hollow
wheel-like cylinder rotating at high speed. Centrifugal
force causes the melt to break up and be exuded horizon-
tally through holes in the vertical circumferential side-
wall of the cylinder or wheel, thus forming so-called pri-
35 mary fibres. These primary fibres are then further
attenuated downward by the action of a suitably controlled
flame or gas stream, thus forming the final glass fibres.

This process has the advantages that the efficiency
of the centrifugation is nearly 100%, and the yield of
glass fibres corresponds to about 95% of the quantity of
melt used. Another advantage of this process is that the
5 product is generally more light-weight than those of the
other processes, and the glass fibres obtained by this pro-
cess are suitable for further processing into the product
commonly known as "glass wool". Disadvantages of this
process are that it is complicated and uneconomical, and,
10 as regards total cost, it is more expensive than the rock-
wool process per unit weight of the product. This is
largely because it requires more expensive starting mate-
rials than does the rock-wool process, and because it
requires a particular melting method.

15   In the flame-attenuation or glass-drawing process,
primary filaments of molten glass are fed into a directed
and controlled stream of gas or steam or into a jet flame
from a burner or blower pipe system. Thinning, lengthening
and division of the filaments into fibres takes place in
20 the flame or the stream of gas or steam. This process is,
however, slow and requires a high energy expenditure.
Moreover, the distribution of fibre diameters is generally
greater than in the other processes, although this process
can be used to produce particularly fine fibres. This pro-
25 cess is not used to a very great extent.

One parameter that has an important influence on the
quality of the product in all the processes is the fluidity
of the molten glass composition at the particular fibrising
temperature being used, and the viscosity of the melt is
30 generally used as a measure of the fluidity. In general,
the lower is the viscosity of the molten glass composition
at a given temperature, the more suitable is the composition
for fibrising at that temperature. This, coupled with
other factors such as those discussed above, has necessi-
35 tated the development of particular glass compositions for
each process.

In particular, as discussed above, the glass compo-

sitions developed for the rock-wool process permit the use
of fly ash and slags as starting materials, whereas it has
not proved possible to utilise such industrial waste
material in the rotary process because the melt would not
5 have properties concomitant with carrying out this process
economically or, in some cases, even at all.

An example of a glass composition that has been
developed especially for the rotary process and is used in
that process is the following composition (percentages are
10 by weight):

SiO_2	59.0%
Al_2O_3	3.4%
Fe_2O_3	0.1%
MgO	5.0%
CaO	8.2%
Na_2O	16.0%
K_2O	1.3%
B_2O_3	7.0%
	100.0%

15

20 This composition is generally considered fairly expensive,
particularly because of the relatively large proportions of
the expensive compounds Na_2O and B_2O_3.

It can be seen that it would be advantageous to
develop a glass composition that permits the use of indus-
25 trial wastes and yet is suitable for use in the rotary pro-
cess and gives fibres of a quality comparable to that of
fibres produced from compositions currently used in the
rotary process. That is to say, it would be advantageous
to be able to combine advantages of the rotary process with
30 those of the rock-wool process. Moreover, it would be
advantageous to develop a glass composition suitable for
use in any of the mentioned fibrising processes.

The present invention provides a glass composition
for the production of fibres comprising the following
35 components in amounts within the respective given ranges
(percentages are by weight):

SiO$_2$	47 to 58%
Al$_2$O$_3$	3 to 12%
Fe$_2$O$_3$	0 to 4%
FeO	0 to 4%
MgO	1 to 6%
CaO	12 to 22%
Na$_2$O	7 to 16%
K$_2$O	0 to 5%
B$_2$O$_3$	0 to 10%
TiO$_2$	0 to 4%
MnO	0 to 4%
BaO	0 to 3%
P$_2$O$_5$	0 to 4%
SO$_3$	0 to 1%
F	0 to 1%

characterised in that the amounts of CaO, Na$_2$O, SiO$_2$, Al$_2$O$_3$
and K$_2$O are such that the following weight ratios are within
the respective given ranges:

CaO : Na$_2$O	0.8 : 1	to 1.8 : 1
SiO$_2$: Al$_2$O$_3$	3.9 : 1	to 8.8 : 1
K$_2$O : Na$_2$O	0	to 0.7 : 1
(CaO/Na$_2$O) : (SiO$_2$/Al$_2$O$_3$)	0.1 : 1	to 0.5 : 1.

This glass composition is suitable for use in any of
the above-mentioned fibrising processes, especially the
rotary or glass-wool process. The composition can utilise
industrial wastes, for example fly ash, blast-furnace slag,
soda-furnace slag and Thomas slag. Moreover, provided that the
K$_2$O : Na$_2$O ratio and other specified ratios are maintained
within the specified ranges, this composition permits the
use of low proportions of Na$_2$O and B$_2$O$_3$. This is especially
important as regards the borax (B$_2$O$_3$) or other boron source,
because the availability of boron is limited and it will
probably become more difficult to obtain and more expensive.

It has been found that the viscosity of a molten
glass composition and the crystallisation tendency or degree
of crystallisation (which should be as low as possible) of
the melt as it solidifies depend largely on the K$_2$O : Na$_2$O

ratio, the CaO : Na_2O ratio, the SiO_2 : Al_2O_3 ratio, and
the (CaO/Na_2O) : (SiO_2 / Al_2O_3) ratio, and that by maintain-
ing these ratios within the specified ranges optimum vis-
cosities and crystallisation tendencies can be achieved.

5 Moreover, by varying these ratios within the given ranges
and/or by varying the amounts of the various components,
these properties may be optimised and regulated to suit the
individual fibrising processes.

Yet in all cases, the glass composition according to
10 the invention can utilise industrial wastes such as those
mentioned above and thus the glass composition according
to the invention is inexpensive and, in particular, is
less expensive than compositions previously developed for
the rotary process. Moreover, energy expenditure required
15 in melting and preparing the glass composition according
to the invention is considerably less than that required
with many known glass compositions because of the low
annealing losses of the raw materials (that is, largely
the industrial wastes) and because these raw materials
20 have already been smelted and oxidised in the processes
from which they are waste products.

The following table indicates the viscosity of a
typical glass composition according to the invention at
various temperatures and compares these values with those
25 for known glass compositions:

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Glass composition	Viscosity of glass composition (log η – dPa.s) at				
	1400°C	1300°C	1200°C	1100°C	1000°C
Typical composition for rotary process	1.46	1.77	2.16	2.64	3.28
Typical composition for rock-wool process	1.26	1.62	CRYSTALLIZATION		
Typical composition for glass-drawing process	–	2.02	2.48	3.08	3.93
Typical composition according to the invention	1.38	1.70	2.11	2.60	3.33

In order for fibrisation to take place without difficulty, the temperature corresponding to log η = 3.0 (where η is the viscosity in decipascal.seconds (dPa.s)) should not exceed 1060°C, otherwise the glass melt may not maintain
5 the requisite fluidity long enough for fibrisation to take place readily or, in other words, the life-time of the fibriser may be insufficient.

It is important that the degree of crystallisation occurring on solidification of the glass composition should
10 be maintained as low as possible because a high degree of crystallisation has an adverse effect on the strength properties of the resulting glass. Moreover, the crystallisation tendency must also be kept low because the occurrence of crystallisation within the centrifugal wheel, in the
15 rotary process, again shortens the life-time of the fibriser. To this end, the crystallisation temperature or liquidus point (L_T) should preferably be low.

In order to achieve the desired regulation of the crystallisation tendency, it is desirable that the ratio
20 CaO : Na_2O should be low while the ratio K_2O : Na_2O should be high. Thus, for example, a high CaO content may be disadvantageous as this tends to increase the crystallisation temperature but, notwithstanding a high CaO content, if the rate of crystallisation is sufficiently low the desired low
25 degree of crystallisation may still be achieved.

The requirement for a high ratio K_2O : Na_2O may necessitate having a high K_2O content but this may be disadvantageous as it tends to decrease the hydrolytic resistance of the glass fibres produced from the glass composi-
30 tion. This can be corrected, however, by the presence of other oxides, such as Fe_2O_3, TiO_2, Al_2O_3 and MnO, which improve the hydrolytic resistance, and slags containing such oxides may be used as a source for these oxides. Moreover, as well as permitting the proportions of K_2O and
35 Na_2O to be raised, the presence of high amounts of oxides that improve the hydrolytic resistance of the product also permits the proportion of B_2O_3 to be lowered without an

adverse effect on the hydrolytic resistance and, as discussed previously, it is advantageous to have a low content of B_2O_3.

In fact, it is an advantage of the glass composi-
5 tions according to the invention that glass fibres produced therefrom generally have an improved hydrolytic resistance as compared with those produced from known glass compositions. The hydrolytic resistance of glass fibres can be measured according to SIS (Swedish
10 Industrial Standard) 13 63 21, in which the amount of alkali dissolved out of ground glass pulp in water at 28^oC is measured by determining the consumption of 0.01 N HCl required to neutralise the alkali. The hydrolytic resistance of known glass fibres, as determined by
15 this method, is generally from 1.0 to 1.5 ml 0.01 N HCl, whereas the hydrolytic resistance of glass fibres produced from the glass composition according to the invention is generally from 0.6 to 1.2 ml 0.01 N HCl.

The following Examples 1 to 3 illustrate glass
20 compositions according to the invention. All parts, percentages and ratios given in the examples are calculated by weight.

Example 1

A glass composition was prepared from:
25   1   part of burnt lime,
0.5 part of blast-furnace slag,
1.7 parts of fly ash,
2   parts of silica sand,
1.2 parts of sodium hydroxide,
30   0.4 part of rasorite,
0.4 part of feldspar and
1.0 part of mill scale.
The resulting composition was as follows:

SiO_2	50.7%
Al_2O_3	7.8%
FeO	3.5%
MgO	2.3%
CaO	18.9%
Na_2O	12.6%
K_2O	1.0%
B_2O_3	2.6%
TiO_2	0.6%
	100.0%

with the following ratios:

CaO	:	Na_2O	1.5	: 1
SiO_2	:	Al_2O_3	6.5	: 1
K_2O	:	Na_2O	0.08	: 1
(CaO/Na_2O)	:	(SiO_2/Al_2O_3)	0.23	: 1

In this composition, the ratio (CaO/Na_2O):
(SiO_2/Al_2O_3) is sufficiently large and the ratio SiO_2 :
Al_2O_3 is sufficiently small to give a composition having
a viscosity of a suitable value to enable fibrisation to
take place readily while giving a product having good
hydrolytic resistance.

The composition has the following viscosity values
η (dPa.s):

$\log \eta$ = 2.0 at $1228^\circ C$

$\log \eta$ = 3.0 at $1046^\circ C$

It can be seen from these values that the desideratum of
the temperature corresponding to $\log \eta$ = 3.0 not exceeding
$1060^\circ C$ is satisfied.

Glass fibres produced from this composition have
properties similar to those produced from known glass com-
positions in the corresponding processes. For example,
when this composition is used for fibrising according to
the rotary process, the properties of the resulting glass
wool are similar to those of glass wool produced by this
process from known glass compositions.

The hydrolytic resistance (Pv) of glass fibres

produced from this composition was found to be 1.1 ml
0.01 N HCl, as determined according to SIS 13 63 21.

It has been found that, despite the high CaO
content in this composition, no crystallisation could be
observed in the glass fibres by either optic or X-ray
means because the rate of crystallisation in the fibris-
ing zone is low. Consequently, the high CaO content with
the resultant high crystallisation temperature, does not
have an adverse effect on the strength of the glass fibres
produced from this composition.

Example 2

The following glass composition was prepared:

SiO_2	49.3%
Al_2O_3	5.8%
Fe_2O_3	3.3%
MgO	2.6%
CaO	13.2%
Na_2O	11.0%
K_2O	4.1%
B_2O_3	6.5%
MnO	2.2%
TiO_2	2.0%
	100.0%

in which the following ratios have the given values:

CaO	:	Na_2O	1.2	:	1
SiO_2	:	Al_2O_3	8.5	:	1
K_2O	:	Na_2O	0.37	:	1
(CaO/Na_2O)	:	(SiO_2/Al_2O_3)	0.14	:	1

This composition had the following properties:
Viscosity η (dPa.s):

$\log \eta$ = 2.0 at $1212^{\circ}C$

$\log \eta$ = 3.0 at $1008^{\circ}C$

Crystallisation temperature
(liquidus point) (L_T) : $995^{\circ}C$
Hydrolytic resistance (PV) of glass fibres:
1.2 ml 0.01 N HCl (SIS 13 63 21).

In this composition, a low crystallisation tempera-
ture is obtained by using a low ratio $CaO : Na_2O$ and a
high ratio $K_2O : Na_2O$, but the decreased hydrolytic resis-
tance that might result from a high content of K_2O is
5 counteracted by the presence of MnO and TiO_2.

Example 3

The following glass composition was prepared:

SiO_2	47.0%
Al_2O_3	8.7%
Fe_2O_3	4.0%
MgO	1.4%
CaO	14.6%
Na_2O	12.2%
K_2O	5.0%
B_2O_3	1.2%
TiO_2	2.3%
MnO	3.6%
	100.0%

in which the following ratios have the given values:

$CaO : Na_2O$	1.2	: 1
$SiO_2 : Al_2O_3$	5.4	: 1
$K_2O : Na_2O$	0.41	: 1
$(CaO/Na_2O) : (SiO_2/Al_2O_3)$	0.22	: 1

This composition had the following properties:

25 Viscosity η (dPa.s):

$\log \eta = 2.0$ at $1231^{\circ}C$

$\log \eta = 3.0$ at $1024^{\circ}C$

Crystallisation temperature
(liquidus point) (L_T) : $1044^{\circ}C$

30 Hydrolytic resistance (PV) of glass fibres:
0.90 ml 0.01 N HCl (SIS 13 63 21).

In this composition, the presence of oxides improv-
ing the hydrolytic resistance, such as Fe_2O_3, TiO_2 and
Al_2O_3, permits the proportions of K_2O and Na_2O to be
35 increased while having a low content of B_2O_3, without
adversely affecting the hydrolytic resistance.

Claims

1.   A glass composition for the production of fibres comprising the following components in amounts within the respective given ranges (percentages are by weight):

SiO_2	47 to 58%
Al_2O_3	3 to 12%
Fe_2O_3	0 to 4%
FeO	0 to 4%
MgO	1 to 6%
CaO	12 to 22%
Na_2O	7 to 16%
K_2O	0 to 5%
B_2O_3	0 to 10%
TiO_2	0 to 4%
MnO	0 to 4%
BaO	0 to 3%
P_2O_5	0 to 4%
SO_3	0 to 1%
F	0 to 1%

characterised in that the amounts of CaO, Na_2O, SiO_2, Al_2O_3 and K_2O are such that the following weight ratios are within the respective given ranges:

CaO	:	Na_2O	0.8 : 1 to 1.8 : 1
SiO_2	:	Al_2O_3	3.9 : 1 to 8.8 : 1
K_2O	:	Na_2O	0 to 0.7 : 1
(CaO/Na_2O)	:	(SiO_2/Al_2O_3)	0.1 : 1 to 0.5 : 1.

2.   A glass composition for the production of fibres characterised in that the following components are present in the respective given amounts (percentages are by weight):

SiO_2	50.7%
Al_2O_3	7.8%
FeO	3.5%
MgO	2.3%
CaO	18.9%
Na_2O	12.6%
K_2O	1.0%
B_2O_3	2.6%
TiO_2	0.6%

3.　　A glass composition for the production of fibres characterised in that the following components are present in the respective given amounts (percentages are by weight):

SiO_2	49.3%
Al_2O_3	5.8%
Fe_2O_3	3.3%
MgO	2.6%
CaO	13.2%
Na_2O	11.0%
K_2O	4.1%
B_2O_3	6.5%
MnO	2.2%
TiO_2	2.0%

4.　　A glass composition for the production of fibres characterised in that the following components are present in the respective given amounts (percentages are by weight):

SiO_2	47.0%
Al_2O_3	8.7%
Fe_2O_3	4.0%
MgO	1.4%
CaO	14.6%
Na_2O	12.2%
K_2O	5.0%
B_2O_3	1.2%
TiO_2	2.3%
MnO	3.6%